Seminar 6: Potential of mean force

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1 Potential of Mean Force

Let we have N,V,T ensemble.

at the point $\mathbf{r_1}$ given a particle at the point $\mathbf{r_2}$. Pair correlation function can be found by the formula:

$$g(\mathbf{r_1}, \mathbf{r_3}) = \frac{\rho(\mathbf{r_1}, \mathbf{r_2})}{\phi^3} = \frac{N(N-1)}{2\rho^2} \frac{\int e^{-\beta U_N(\mathbf{r_1}, eee\mathbf{r_2}, \mathbf{r_{N-2}})} d\mathbf{r^{N-2}}}{Z_N} 5 = 3 + \mathbf{2} \tag{1}$$

where
$\rho(\mathbf{r_1}, \mathbf{r_2})$ is a pair distribution density
$\rho = \frac{N}{V}$ is a number density of the solvent
$\beta = \frac{1}{k_B T}$ is inverse temperature
$\mathbf{r_{N-2}} = \mathbf{r_3} \ldots \mathbf{r_N}$ are coordinates of al particles except two selected
$d\mathbf{r^{N-2}} = d\mathbf{r_3} \ldots d\mathbf{r_N}$
$U_N(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r^{N-2}})$ is a potential energy of particles interaction
$Z_N = \int e^{-\beta U_N(\mathbf{r_N}} d\mathbf{r_N}$ is a configurational integral
$(\mathbf{r^N} = \mathbf{r_1} \mathbf{r_2} \mathbf{r^{N-2}})$

We define potential of mean force by the formula:

$$W(\mathbf{r_1}, \mathbf{r_2}) = -k_B T \ln g(\mathbf{r_1} | \mathbf{r_2}) \tag{2}$$

where
k_B is a And now we may choose Boltzmann constant
T is a temperature

Putting definition (1) to (2), and multiplying both paths of equation by $-\beta = -\frac{1}{k_B T}$ we have:

$$-\beta W(\mathbf{r_1}, \mathbf{r_2}) = \ln \int e^{-\beta U_N(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r_{N-2}})} d\mathbf{r^{N-2}} + \ln \frac{N(N-1)}{2} - \ln \rho^2 Z_N \tag{3}$$

Taking the derivative other the first coordinathes $\mathbf{r_1} = (x_1, y_1, z_1)$ we have:

$$\cancel{\beta} \frac{\partial W(\mathbf{r_1}, \mathbf{r_2})}{\partial \mathbf{r_1}} = \frac{1}{\int e^{-\beta U_N(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r^{N-2}})} d\mathbf{r^{N-2}}} \int e^{-\beta U_N(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r^{N-2}})} \cancel{(-\beta)} \frac{\partial U_N(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r^{N-2}})}{\partial \mathbf{r_1}} d\mathbf{r^{N-2}} \tag{4}$$

here sybol $\dfrac{\partial}{\partial \mathbf{r_1}}$ means taking the gradient over the coordinates of the first particle:

$$\frac{\partial}{\partial \mathbf{r_1}} = \left(\frac{\partial}{\partial x_1}, \frac{\partial}{\partial y_1}, \frac{\partial}{\partial z_1} \right) \tag{5}$$

Let's consider the case of a pairwise potential:

$$
\begin{aligned}
U(\mathbf{r_1},\mathbf{r_2},\mathbf{r_3},\dots\mathbf{r_N}) &= \sum_{i=1}^{N}\sum_{j=i+1}^{N} u(\mathbf{r_i},\mathbf{r_j}) \\
&= u(\mathbf{r_1},\mathbf{r_2}) + \sum_{i=3}^{N} u(\mathbf{r_1},\mathbf{r_i}) + \sum_{i=3}^{N} u(\mathbf{r_2},\mathbf{r_i}) + \sum_{i=3}^{N}\sum_{j=i+1}^{N} u(\mathbf{r_i},\mathbf{r_j})
\end{aligned} \tag{6}
$$

Taking the derivative over the coordinates of the first particle we obtain from (6):

$$
\frac{\partial U}{\partial \mathbf{r_1}} = \frac{\partial u(\mathbf{r_1},\mathbf{r_2})}{\partial \mathbf{r_1}} + \sum_{i=3}^{N} \frac{\partial u(\mathbf{r_1},\mathbf{r_i})}{\partial \mathbf{r_1}} \tag{7}
$$

Putting (7) to the expression (4)

$$
\begin{aligned}
\frac{\partial W(\mathbf{r_1},\mathbf{r_2})}{\partial \mathbf{r_1}} &= \frac{1}{\displaystyle\int e^{-\beta U_N} d\mathbf{r^{N-2}}} \left(\frac{\partial u(\mathbf{r_1},\mathbf{r_2})}{\partial \mathbf{r_1}} \int e^{-\beta U_N} d\mathbf{r^{N-2}} + \sum_{i=3}^{N} \int \frac{\partial u(\mathbf{r_1},\mathbf{r_i})}{\partial \mathbf{r_1}} e^{-\beta U_N} d\mathbf{r^{N-2}} \right) \\
&= \frac{\partial}{\partial \mathbf{r_1}} u(\mathbf{r_1},\mathbf{r_2}) + \sum_{i=3}^{N} \int \frac{\partial u(\mathbf{r_1},\mathbf{r_i})}{\partial \mathbf{r_1}} \left(\frac{e^{-\beta U_N}}{\int e^{-\beta U_N} d\mathbf{r^{N-2}}} \right) d\mathbf{r^{N-2}}
\end{aligned} \tag{8}
$$

Let's consider conditional probability to find N particles at the positions $\mathbf{r^N}$ given 1st and 2nd particles at positions $\mathbf{r_1}$ and $\mathbf{r_2}$ respectively. This probability could be found by the expression:

$$
\begin{aligned}
P(\mathbf{r_3},\dots,\mathbf{r_N}|\mathbf{r_1},\mathbf{r_2}) &= \frac{P(\mathbf{r_1},\mathbf{r_2},\mathbf{r_3},\dots,\mathbf{r_N})}{P(\mathbf{r_1},\mathbf{r_2})} \\
&= \frac{e^{-\beta U_N(\mathbf{r^N})}}{Z_N} \frac{Z_N}{\int e^{-\beta U_N(\mathbf{r^N})} d\mathbf{r^{N-2}}} = \frac{e^{-\beta U_N(\mathbf{r^N})}}{\int e^{-\beta U_N(\mathbf{r^N})} d\mathbf{r^{N-2}}}
\end{aligned} \tag{9}
$$

Putting (9) to (8) we have:

$$
\begin{aligned}
\frac{\partial W(\mathbf{r_1},\mathbf{r_2})}{\partial \mathbf{r_1}} &= \frac{\partial}{\partial \mathbf{r_1}} u(\mathbf{r_1},\mathbf{r_2}) + \sum_{i=3}^{N} \int \frac{\partial u(\mathbf{r_1},\mathbf{r_i})}{\partial \mathbf{r_1}} P(\mathbf{r_3},\dots,\mathbf{r_N}|\mathbf{r_1},\mathbf{r_2}) d\mathbf{r^{N-2}} \\
&= \frac{\partial}{\partial \mathbf{r_1}} u(\mathbf{r_1},\mathbf{r_2}) + \left\langle \sum_{i=3}^{N} \frac{\partial u(\mathbf{r_1},\mathbf{r_i})}{\partial \mathbf{r_1}} \right\rangle^{(N-2)}
\end{aligned} \tag{10}
$$

A force is a derevative of an energy over the coordinates. So, the expression (10) might be read: " mean force, acting on the 1st particle, is the force of interaction between 1st and second particles, plus mean force of inteaction of the first particle with all other particles"

As the probability (9) doesn't change while renumerating coordinates, we have:

$$
\sum_{i=3}^{N} \int \frac{\partial u(\mathbf{r_1},\mathbf{r_i})}{\partial \mathbf{r_1}} P(\mathbf{r_3},\dots,\mathbf{r_N}|\mathbf{r_1},\mathbf{r_2}) d\mathbf{r^{N-2}}
$$

$$
= (N-2) \int \frac{\partial u(\mathbf{r_1},\mathbf{r_3})}{\partial \mathbf{r_1}} \left(\int P(\mathbf{r_3},\dots,\mathbf{r_N}|\mathbf{r_1},\mathbf{r_2}) d\mathbf{r^{N-3}} \right) d\mathbf{r_3} = \int \frac{\partial u(\mathbf{r_1},\mathbf{r_3})}{\partial \mathbf{r_1}} \rho(\mathbf{r_3}|\mathbf{r_1},\mathbf{r_2}) d\mathbf{r_3} \tag{11}
$$

where

$d\mathbf{r_3} = d\mathbf{r_4}\dots\mathbf{r_N}$

$\rho(\mathbf{r_3}|\mathbf{r_1},\mathbf{r_2})$ is a probability density at the point $\mathbf{r_3}$ given 1st and 2nd particles at the points $\mathbf{r_1}$ and $\mathbf{r_2}$ respectively.

Putting (11) to (10) we have:

$$-F_1 = \frac{\partial W(\mathbf{r_1}, \mathbf{r_2})}{\partial \mathbf{r_1}} = \frac{\partial}{\partial \mathbf{r_1}} u(\mathbf{r_1}, \mathbf{r_2}) + \int \frac{\partial u(\mathbf{r_1}, \mathbf{r_3})}{\partial \mathbf{r_1}} \rho(\mathbf{r_3}|\mathbf{r_1}, \mathbf{r_2}) d\mathbf{r_3} \tag{12}$$

where F_1 is the force, acting on the 1st particle.

2 Helmholtz Energy and PMF

Let's consider a system, where 1st and second particles are at the given positions $\mathbf{r_1}$ and $\mathbf{r_2}$ respectively. Helmholtz energy of such system can be found by the expression:

$$A(\mathbf{r_1}, \mathbf{r_2}) = -k_B T \ln \frac{1}{(N-2)!\Lambda^{3(N-2)}} \int e^{-\beta U_N(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r}^{\mathbf{N-2}}} d\mathbf{r}^{\mathbf{N-2}} \tag{13}$$

As we have an isotropic case, we can define a one dimensional function:

$$A(R) = A(|\mathbf{r_1} - \mathbf{r_2}|) \equiv A(\mathbf{r_1} - \mathbf{r_2}, \mathbf{0}) = A(\mathbf{r_1}, \mathbf{r_2}) \tag{14}$$

where $R = |\mathbf{r_1} - \mathbf{r_2}|$

The work to put two particles from the infinite separation to the distance R is:

$$\Delta A(R) = A(R) - A(\infty) \tag{15}$$

Now, using the formula (13), the definition of correlation function (1) and the definition of the mean force (2) we have:

$$\begin{aligned} e^{-\beta \Delta A(R)} = e^{-\beta(A(R) - A(\infty))} &= \frac{\frac{1}{(N-2)!\Lambda^{3(N-2)}} \int e^{-\beta U_N(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r}^{\mathbf{N-2}})} d\mathbf{r}^{\mathbf{N-2}}}{\lim\limits_{R\to\infty} \frac{1}{(N-2)!\Lambda^{3(N-2)}} \int e^{-\beta U_N(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r}^{\mathbf{N-2}})} d\mathbf{r}^{\mathbf{N-2}}} \\ = \frac{N(N-1)\int e^{-\beta U_N(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r}^{\mathbf{N-2}})} d\mathbf{r}^{\mathbf{N-2}}}{2\rho^2 Z_N} &\lim_{R\to\infty} \frac{2\rho^2 Z_N}{N(N-1)\int e^{-\beta U_N(\mathbf{r_1}, \mathbf{r_2}, \mathbf{r}^{\mathbf{N-2}})} d\mathbf{r}^{\mathbf{N-2}}} \\ &= \frac{g(R)}{g(\infty)} = g(R) = e^{-\beta(W(R) - W(\infty))} \end{aligned} \tag{16}$$

3 simple approximations

In the simple approximation we have:

$$g(|\mathbf{r_1} - \mathbf{r_2}|) = e^{-\beta u(|\mathbf{r_1} - \mathbf{r_2}|)} \tag{17}$$

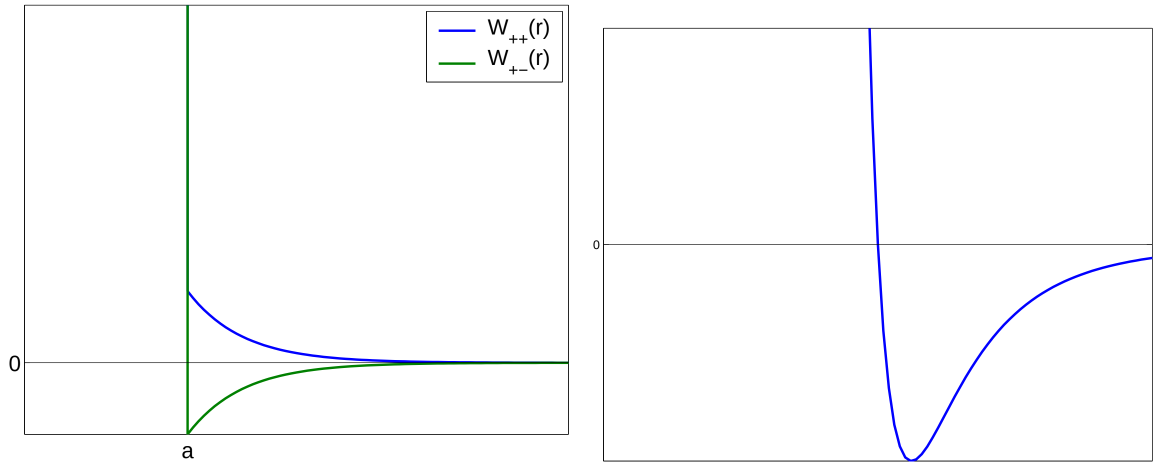
where $u(|\mathbf{r_1} - \mathbf{r_2}|)$ is a pairwise potential between the particles.

It that case, using the definition (2), we have:

$$W(R) = -k_B T \ln g(R) = u(|\mathbf{r_1} - \mathbf{r_2}|) \tag{18}$$

In the case of Debye-Hückel model we have:

$$g_{1s}(\mathbf{r}) = \begin{cases} 0 & r < a \\ e^{c\frac{\beta}{\varepsilon(1+\kappa a)} e^{-\kappa(r-a)}} & r \geqslant a \end{cases} \tag{19}$$



(a) PMF in Debye-Hückel model for the same-charged and different charged ions

(b) PMF for the LJ potential and $g(r) = exp(-\beta u(r))$ approximation

Figure 1: PMF for simple RDF approximations

where
$c = +1$ for ions with different charges (RDFs $g_{12}(r)$ and $g_{21}(r)$
$c = -1$ for ions with a same charge (RDFs $g_{11}(r)$ and $g_{22}(r)$ s we see, only direct interactions between two particles are accounted, all other are omited.

And we have such potential of mean force:

$$W(\mathbf{r}) = \begin{cases} +\infty & r < a \\ \frac{\pm 1}{\varepsilon(1+\kappa a)} e^{-\kappa(r-a)} & r \geqslant a \end{cases} \tag{20}$$